

**A Survey of the Water Quality of Streams in the Primary Region of  
Mountain Top Removal / Valley Fill Coal Mining**

**August 20, 1999**

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**Approvals/Signatures**

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Environmental Services Division Project Officer - William Hoffman  
USEPA, Philadelphia, PA

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USEPA, Fort Meade, MD

1. **Project Name:** A Survey of Stream Water Quality in the Primary Region of Mountain Top Removal/ Valley Fill Coal Mining
2. **Project Requested by:** William Hoffman  
Environmental Services Division  
USEPA, Philadelphia, PA
3. **Date of Request:** August 1999
4. **Date of Project Initiation:** August 1999
5. **Project Officer:** William Hoffman,  
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Environmental Services Division  
Associate Director of Science  
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7. **Project Description:**

#### **A. Objective and Scope**

A typical mountain top removal/valley fill (MTR/VF) mining operation in the Appalachian coal fields removes overburden and interburden material to facilitate the extraction of coal. Excess spoils are often placed in adjacent valleys containing first and second order streams. The effect of these mining operations on the water quality of downstream reaches is uncertain.

This project will supplement existing data on stream water quality at and downstream of MTR/VF operations. The study has two objectives:

- C Characterize and compare conditions in three categories of streams:
  - 1) streams that are not mined;
  - 2) streams in mined areas with valley fills; and
  - 3) streams in mined areas without valley fills.
- C Characterize conditions and describe any cumulative impacts that can be detected in streams downstream of multiple fills.

This study will use measures of flow rate, field chemistry parameters, and laboratory analyses of selected parameters to characterize stream water quality at these sites. The study will provide data and information

for the Programmatic Environmental Impact Statement (PEIS). The PEIS is scheduled for completion in December 2000.

This study compliments the aquatic biology study underway for this same region as part of the PEIS. Stream water chemistry sample sites will correspond to sites where biological samples are being collected. The chemistry data will be useful in better understanding the biological data.

## **B. Data Usage**

This section describes the stream water chemistry indicators and how the data will be used in the assessment of stream condition. For descriptions of methods, sampling frequencies, preservatives, etc., see Section D.

The chemical concentrations and flow rates will be used to identify parameters of concern for toxicity and adverse stream conditions. This will be done through comparison of existing conditions with stream water quality criteria. West Virginia has stream water quality criteria for three categories: warm water fishery, cold water fishery, and drinking water. The applicable warm and cold water fishery water quality criteria limits are identified to assist in setting method detection limits for laboratory analyses. These criteria limits are included in the table below.

<i><b>Parameter</b></i>	<i><b>Water Quality Criteria Limit</b></i>
Total Aluminum	750 ug/L
Total Beryllium	130 ug/L
Dissolved Oxygen	minimum 5.0 mg/L - field measure
Total Iron	1,500 ug/L
Mercury	2.4 ug/L
pH	6.0 to 9.0 standard units - field measure
Total Selenium	5 ug/L
Chloride	230 mg/L

The data will also be used to develop a synoptic description of stream water chemistry in the primary region of MTR/VF operations. Cumulative effects of pollutants will be evaluated using pollutant loadings calculated from flow rate and concentration data.

The sampling sites are located in unmined watersheds, mined watersheds with valley fills, and mined watersheds without valley fills. The mined watersheds with valley fills represent a gradient of attributes including the number of fills, size of fills, age of fills, and the percentage of the total watershed filled. The

mined watersheds without valley fills also represent various conditions (e.g. old contour mining and underground mines). The measurements of stream condition will be compared to the watershed attributes associated with mining to explore any relationship between stream condition and those attributes.

Water chemistry and loadings will be analyzed to determine the condition of all sites. The data from the mined sites will be grouped and compared to the values from the group of unmined sites to determine impacts from the MTR/VF operations.

Some sites were chosen on larger streams where MTR/VF operations could be bracketed by upstream and downstream sites (e.g. Mud River). Control sites in the larger streams, upstream of large MTR/VF operations will be compared to sites downstream of the operations to determine whether there are any significant differences between the upstream control site and the site downstream of the mining operations. Some of the sites upstream of the MTR/VF operations are subject to other sources of impairment in the headwaters (e.g. residential development).

An estimate of precision will help to determine significant differences between sites. The estimate of precision will be based on field duplicate samples. Any difference in values between sites that is larger than the laboratory's analytical precision will be considered a significant difference. Analysis of the values for unmined sites and possible other reference values, will determine whether the difference indicates impairment of the stream water chemistry.

The watersheds represent a gradient of conditions in terms of the age of fills, size of fills, number of fills, and the percentage of the watershed filled. To the extent possible, relationships between these attributes and the stream chemistry data will be explored.

## **Stream Flow Rate**

Stream flow rate will be measured at or near the sample point using standard techniques recommended by the USGS and the EPA (see reference section). The data shall be recorded on the field form included as Appendix B. If it is a wadable stream, USGS flow measurement protocol may be used, including a top setting rod and a single axis electromagnetic velocity meter. The electromagnetic velocity meter will be used in place of the mechanical velocity meters usually employed by USGS staff. If permanent weirs or staff gages are installed at the sampling sites so as to allow quick measurement of the head on the weir or the stage of the stream, those shall be acceptable for stream measurement values. Very small flows will be measured with a calibrated bucket and stop watch if it takes more than ten seconds to fill the bucket.

## **Field Measurements of Water Chemistry**

Streams will be sampled for dissolved oxygen, conductivity, pH and temperature in the field, *in situ*. Commercial electrometric probes and meters will be calibrated to reference solutions in the field and used

in a standard approved procedure (See Section 13). The sample and calibration data will be entered in the Field Sheet -Water Sampling, Appendix A.

### **C. Monitoring Design and Rationale**

Monitoring sites were chosen to meet the objectives of the study as outlined above. The monitoring sites, stream name, watershed name, approximate location and approximate description of mining activity upstream of the sites are provided in Table 1. The term “inactive mining” means no current extraction is occurring.

Note that the station numbers in Table 1 are not sequential. The thirty-seven (37) benthic sampling sites were chosen from a larger pool of candidate sampling sites (a total of 127 sites).

This survey was designed to provide a synoptic description of stream conditions in five watersheds across the primary MTR/VF region. These watersheds are Twentymile Creek, Clear Fork, Island Creek, upper Mud River and Spruce Fork. Within each watershed, two arrays of streams were selected by staff familiar with the mining operations in the watershed (primarily WV DEP mining inspectors and the Streams Workgroup working on the PEIS). One stream array in each watershed is unmined. The other stream array in each watershed contains significant MTR/VF operations. The MTR/VF operations represent a gradient of number and size of fills, type of fills, and age of fills. A paired-watershed approach was used to locate some of the sites so that some of the unmined and mined sites within a watershed would be similar in terms of approximate watershed area and elevation. In addition, a few sites have mining activity in the upstream watershed, but no valley fills.

Several sediment control structures were considered as candidate monitoring sites. However, many of the sites were not reconstructed streams, but ponds or dry ditches filled with boulder-sized rip-rap. Only one of the sediment control structure sites had flowing water.

<b>Table 1. Station Locations and Descriptions</b>				
<b>Station Number</b>	<b>Stream Name</b>	<b>Watershed</b>	<b>Approximate Locations</b>	<b>Description of Mining Activity Upstream</b>
MT01	Mud River	Mud River	Approximately 650 feet downstream of confluence with Rushpatch Branch.	Mined

<b>Table 1. Station Locations and Descriptions</b>				
<b>Station Number</b>	<b>Stream Name</b>	<b>Watershed</b>	<b>Approximate Locations</b>	<b>Description of Mining Activity Upstream</b>
MT02	Rushpatch Branch	Mud River	Approximately 500 feet upstream of confluence with Mud River.	Unmined
MT03	Lukey Fork	Mud River	Approximately 1 mile upstream of confluence with Mud River.	Unmined
MT13	Spring Branch of Ballard Fork	Mud River	Approximately 585 feet upstream of confluence with Ballard Fork.	Unmined
MT14	Ballard Fork	Mud River	Approximately 900 feet upstream of confluence with Mud River	Active mining. Site is downstream of 8 valley fills.
MT15	Stanley Fork	Mud River	Approximately 700 feet upstream of confluence with Mud River.	Inactive mining. Site is downstream of 6 valley fills.
MT18	Sugartree Branch	Mud River	Approximately 2000 feet upstream of confluence with Mud River.	Inactive mining. Site is downstream of 2 valley fills.
MT23	Mud River	Mud River	Approximately 1300 feet downstream of confluence with Connelly Branch.	Cumulative downstream site for Mud River. Downstream of active mining and 26 valley fills.
MT24	Stanley Fork	Mud River	Stanley Fork Drainage, Sediment Control Structure	Inactive mining. Site is located in a sediment control structure on top of fill.

<b>Table 1. Station Locations and Descriptions</b>				
<b>Station Number</b>	<b>Stream Name</b>	<b>Watershed</b>	<b>Approximate Locations</b>	<b>Description of Mining Activity Upstream</b>
MT25B	Rockhouse Creek	Spruce Fork	Approximately 1.2 miles upstream of confluence with Spruce Fork. Downstream of pond.	Inactive mining. Site is downstream of 1 valley fill.
MT32	Beech Creek	Spruce Fork	Approximately 1.9 miles upstream of confluence with Spruce Fork.	Inactive mining. Site is downstream of 5 valley fills.
MT34B	Left Fork of Beech Creek	Spruce Fork	Approximately 900 feet upstream of confluence with Beech Creek. Downstream of pond.	Active mining. Site is downstream of 1 valley fill.
MT39	White Oak Branch	Spruce Fork	Approximately 2000 feet upstream of confluence with Spruce Fork.	Unmined
MT40	Spruce Fork	Spruce Fork	In Blair, directly upstream of confluence with White Trace Branch.	Upstream control for Spruce Fork. Downstream of inactive mining and 9 valley fills, including 2 refuse fills.
MT42	Oldhouse Branch	Spruce Fork	Approximately 2400 feet upstream of confluence with Spruce Fork.	Unmined
MT45	Pigeonroost Branch	Spruce Fork	Approximately 4500 feet upstream of confluence with Spruce Fork.	Inactive Mining. No valley fills.

<b>Table 1. Station Locations and Descriptions</b>				
<b>Station Number</b>	<b>Stream Name</b>	<b>Watershed</b>	<b>Approximate Locations</b>	<b>Description of Mining Activity Upstream</b>
MT48	Spruce Fork	Spruce Fork	Approximately 5100 feet downstream of confluence with Beech Creek.	Cumulative downstream site for Spruce Fork. Downstream of active mining and 22 valley fills.
MT50	Cabin Branch	Island Creek	Approximately 650 feet upstream of confluence with Jack's Fork.	Unmined
MT51	Cabin Branch	Island Creek	Approximately 1800 feet upstream of confluence with Copperas Mine Fork.	Unmined
MT52	Cow Creek	Island Creek	Approximately 3 miles upstream of confluence with Left Fork.	Upstream control for Cow Creek, but is influenced by inactive mining.
MT55	Cow Creek	Island Creek	Approximately 1000 feet downstream of confluence with Left Fork.	Cumulative downstream site for Cow Creek. Site is downstream of inactive mining and 4 valley fills.
MT57B	Hall Fork	Island Creek	Approximately 3600 feet upstream of Left Fork. Downstream of pond effluent.	Inactive mining. Site is downstream of 1 valley fill.
MT60	Left Fork	Island Creek	Approximately 5000 feet upstream of confluence with Cow Creek.	Inactive mining. Site is downstream of 2 valley fills.



<b>Table 1. Station Locations and Descriptions</b>				
<b>Station Number</b>	<b>Stream Name</b>	<b>Watershed</b>	<b>Approximate Locations</b>	<b>Description of Mining Activity Upstream</b>
MT62	Toney Fork	Clear Fork	Approximately 300 feet downstream of confluence with Buffalo Fork.	Inactive mining. Site is downstream of 10 valley fills.
MT64	Buffalo Fork	Clear Fork	Approximately 4900 feet upstream of confluence with Toney Fork.	Inactive mining. Site is downstream of 5 valley fills.
MT69	Ewing Fork	Clear Fork	Approximately 2000 feet upstream of confluence with Toney Fork.	Mined
MT75	Toney Fork	Clear Fork	Approximately 700 feet downstream of Reeds Branch.	Inactive mining. Site is downstream of 5 valley fills.
MT78	Raines Fork	Clear Fork	Approximately 400 feet upstream of confluence with Sycamore Creek.	Inactive mining. No fills.
MT79	Davis Fork	Clear Fork	Approximately 600 feet upstream of confluence with Sycamore Creek.	Unmined?
MT81	Sycamore Creek	Clear Fork	Approximately 500 feet upstream of confluence with Lem Fork.	Mined
MT86	Rader Fork	Twentymile Creek	Approximately 500 feet upstream of confluence with Twentymile Creek.	Cumulative downstream site for Rader Fork. Inactive mining. Site is downstream of 3 valley fills.

<b>Table 1. Station Locations and Descriptions</b>				
<b>Station Number</b>	<b>Stream Name</b>	<b>Watershed</b>	<b>Approximate Locations</b>	<b>Description of Mining Activity Upstream</b>
MT87	Neff Fork	Twentymile Creek	Approximately 800 feet upstream of confluence with Rader Fork.	Inactive mining. Site is downstream of 3 valley fills and a mine drainage treatment plant.
MT91	Rader Fork	Twentymile Creek	Approximately 500 feet upstream of confluence with Neff Fork.	Upstream control for Rader Fork. Unmined
MT95	Neil Branch	Twentymile Creek	Approximately 500 feet upstream of confluence with Twentymile Creek.	Unmined
MT98	Hughes Fork	Twentymile Creek	Approximately 200 feet upstream of confluence with Jim's Hollow.	Inactive mining. Site is downstream of 8 valley fills.
MT103	Hughes Fork	Twentymile Creek	Approximately 2500 feet upstream of confluence with Jim's Hollow.	Inactive mining. Site is downstream of 6 valley fills.
MT104	Hughes Fork	Twentymile Creek	Approximately 1.3 miles upstream of confluence with Bells Fork. Downstream of pond on mainstem of Hughes Fork.	Inactive mining. Site is downstream of 8 valley fills.

#### **D. Monitoring Parameters, Sampling Methods and Their Frequency of Collection**

Appendix A is a copy of the field sheet which will be used at each site and on each occasion when water chemistry is being measured. The elements of the field sampling sheet that are completed in the field include:

station number, location, date, time, investigators, agency, pH, temperature, D.O., conductivity, chain-of-custody, number of sample containers & preservatives, and comments and observations. It should also contain the calibration measurements for the field meters whenever they are calibrated (see Section 13).

Appendix B is a copy of the form which is to be used when stream flow is being calculated from area/velocity measurements. The elements of the flow measurement sheet which are to be completed in the field include: station number, location, date, time, investigators, agency, and the table of values for distance, depth, velocity measured across the stream.

### Field Measurements of Water Chemistry

Dissolved oxygen, conductivity, temperature, and pH are measured in situ using an electrometric field meter. The field chemistry measurements are taken at each sampling site and shall be consistent with EPA Method 360.1 for dissolved oxygen, EPA Method 120.1 for specific conductance, EPA Method 170.1 for temperature, and EPA Method 150.1 for pH.

### Aqueous Sample Collection and Shipping

The laboratory will provide sample containers, acid and base preservatives, labels, and shipping containers. They will be shipped to the WVDEP field offices where the inspectors are located. A laboratory staff person will participate in the training event for inspectors to explain field duplicate samples, field filtration (see appendix A), field blanks (see appendix A, filtration blanks), preservatives, and other QA procedures to be followed. Inspectors will take the sample containers and shipping containers to the sample site and fill them following the protocol consistent with the 40 CFR Part 136 (containers, preservatives and holding times). They will store the samples on ice in the shipping containers until they are ready to ship to the lab.

They will add ice, where appropriate, to the containers and seal them following chain-of-custody procedures. Samples will be shipped by Federal Express in time to permit the lab to receive the samples and perform the analyses within the appropriate holding time. The laboratory shall verify that preservation of samples checking pH and temperature.

## E. Parameter Table

Table 2. Parameters				
Parameter	Method *	"Frequency of Collection	Sample Preservation/Holding Time (ice to < 4C, acid to pH<2)	Method Detection Limits** (ug/l)
Flow Rate	USGS stream gaging protocol modified to use electromagnetic velocity meter	On each sampling occasion at all 37 sites	not applicable	not applicable

Table 2. Parameters				
Parameter	Method *	"Frequency of Collection	Sample Preservation/Holding Time (ice to < 4C, acid to pH<2)	Method Detection Limits** (ug/l)
Temperature (°C),	<b>EPA 170.1</b> [Hydrolab type multiparameter field meter, <i>in situ</i> . See Section D.]	On each sampling occasion at all 37 sites	not applicable, <i>in situ</i>	not applicable
Dissolved Oxygen*** (mg/l),	EPA 360.1 [in situ]	On each sampling occasion at all 37 sites	not applicable, <i>in situ</i>	not applicable (Capable of ± 0.2 mg/L*)
pH*** (su),	EPA 150.1 [in situ]	On each sampling occasion at all 37 sites	not applicable, <i>in situ</i>	not applicable (Capable of measuring +/- 0.2 SU*)
Conductivity (umhos/cm)	EPA 120.1 [in situ]	On each sampling occasion at all 37 sites	not applicable, <i>in situ</i>	not applicable
Total Suspended Solids	EPA 160.2	Monthly	Ice/7 days	5000
Total Dissolved Solids	EPA 160.1	Monthly	Ice/7 days	5000
Acidity	EPA 305.1	Monthly	Ice/14 days	2000
Alkalinity	EPA 310.1	Monthly	Ice/14 days	4000
Sulfate	EPA 375.4	Monthly	Ice/28 days	10000
Nitrate+Nitrite	EPA 300.0 Unless acid preservative interferes	Monthly	Ice/H <sub>2</sub> SO <sub>4</sub> /28 Days	100
Total Phosphorous	EPA 365.4	Monthly	Ice/H <sub>2</sub> SO <sub>4</sub> /28 Days	10
Total Organic Carbon	EPA 415.1	Monthly	Ice/H <sub>2</sub> SO <sub>4</sub> /28 Days	1000
Dissolved Organic Carbon	EPA 415.1	Monthly	Field filtered (see Appendix A) Ice/H <sub>2</sub> SO <sub>4</sub> /28 Days	1000
Dissolved Metals Al, Fe, Mn	EPA 200.7	Monthly	Field filtered (see Appendix A) Ice/HNO <sub>3</sub> /6 months	100
Chloride***	EPA 300.0	Monthly	Ice/28 days	80000

Table 2. Parameters				
Parameter	Method *	"Frequency of Collection	Sample Preservation/Holding Time (ice to < 4C, acid to pH<2)	Method Detection Limits** (ug/l)
Total K, Na	EPA 258.1, 273.1	Monthly	Ice/HNO <sub>3</sub> /6 months	1000
Total Al***	EPA 200.7	Monthly	Ice/HNO <sub>3</sub> /6 months	250
Ca, Mg, Mn	EPA 200.7	Monthly	Ice/HNO <sub>3</sub> /6 months	100
Hardness	EPA 200.7 (Calculated from Ca + Mg) 2340B APHA	Monthly	Ice/HNO <sub>3</sub> /6 months	Not Applicable
Total, Cr, Zn	EPA 200.7	Monthly	Ice/HNO <sub>3</sub> /6 months	10
Total Ag	EPA 200.7	Monthly	Ice/HNO <sub>3</sub> /6 months	10
Total Cu	EPA 200.7	Monthly	Ice/HNO <sub>3</sub> /6 months	10
Total Fe***	EPA 200.7	Monthly	Ice/HNO <sub>3</sub> /6 months	500
Total Ni	EPA 200.7	Monthly	Ice/HNO <sub>3</sub> /6 months	10
Total Be***	EPA 200.7	Monthly	Ice/HNO <sub>3</sub> /6 months	40
Total As	EPA 200.7	Monthly	Ice/HNO <sub>3</sub> /6 months	5
Total Cd	EPA 200.7	Monthly	Ice/HNO <sub>3</sub> /6 months	5
Total Pb	EPA 200.7	Monthly	Ice/HNO <sub>3</sub> /6 months	5
Total Se***	EPA 200.7	Monthly	Ice/HNO <sub>3</sub> /6 months	2
Total Sb	EPA 200.7	Monthly	Ice/HNO <sub>3</sub> /6 months	5
Total Tl	EPA 200.7	Monthly	Ice/HNO <sub>3</sub> /6 months	5
Total Hg***	EPA 245.1	Monthly	Ice/HNO <sub>3</sub> /6 months	0.8

\*Other equivalent 40CFR Part 136 Methods may be substituted in order to meet the needed Method Detection Limits listed.

\*\*The method detection limits listed are not critical if ambient levels are routinely measured at significantly higher levels. If the detection levels listed for WVVQSC analytes can not be achieved and the routine ambient levels are not detectable, the Project Officer must be notified.

\*\*\* Denotes parameter with applicable West Virginia Water Quality Stream Criteria (WVVQSC) for aquatic life.

## 8. Schedule of Tasks and Products

Table 3. Schedule of Tasks and Products														
Activities for period 09/99-09/00	9	10	11	12	1	2	3	4	5	6	7	8	9	10
Sampler Training	X	X												
Monthly Sampling	X	X	X	X	X	X	X	X	X	X				
Data analysis and report preparation					X	X	X	X	X	X	X	X	X	
Final report due to USEPA and Gannett Fleming when project completed														X

## 9. Project Organization and Responsibility

EPA Region III, Environmental Services Division

Office of Environmental Programs

William Hoffman (Project Officer, coordination of multiple agencies, & contractors)

Gary Bryant, Scott McPhillamy (draft Work Plan, data compilation and field operations evaluation team)

Office of Analytical Services and Quality Assurance

Patricia Krantz (Office Director) and Joseph Slayton (Associate Director of Science)

Office of Analytical Services and Quality Assurance (QA review)

U.S. Army Corps of Engineers, Huntington District

George Kincaid (sampler training & support, data compilation and evaluation team)

U.S. Geological Survey, West Virginia

Ronald Evaldi (training inspectors in flow measurement)

WV Department of Environmental Protection

Office of Mining & Reclamation

John Ailes (Office Chief)  
Joe Parker, Deputy Chief (oversee mine inspectors who collect samples)  
Bill Simmons, Logan Office, (oversees mine inspectors who collect samples)  
Dan Bays, Inspector (sites MT01, 02, 03, 13, 14, 15, 18, 23, 24)  
Ray Horricks, Inspector (sites MT39, 40 42, 45, 48, 32, 25B, 34B)  
Darryl O'Brien, Inspector (sites MT49, 51, 52, 57B, 60, 55)  
Joe Lockery, Inspector (sites MT78, 79, 81)  
Tom Woods, Inspector (sites MT62, 64, 69, 75)  
Bill Little, Inspector (sites MT86, 87, 91, 95)  
Pat Lewis, Inspector (sites MT98, 103, 104)

#### Signal Corporation

Hope Childers (database manager, data interpretation, GIS support)

Contract Laboratory - provide chemical data and supporting documentation. The commercial laboratory employed since August 1999 is the National Research Center for Coal and Energy, P.O. Box 6064, Evansdale Drive, Morgantown, WV 26506-6064. David L. Brant is the Laboratory Director.

## 10. Data Quality Requirements and Assessments

**Field duplicate samples will be collected at 10% of the sites on each sampling occasion (one field duplicate per sampling crew per day).** This field duplicate will be processed as an independent sample in the laboratory and will be reported like other field samples.

The field duplicates will be used to estimate precision of the sampling method. The estimate of precision includes error associated with field collections at the site and error associated with laboratory activities as well as true variation in the water being sampled. Since it is not possible to separate the true variation from the sampling error, this estimate of precision is not wholly composed of estimates of "measurement error".

Precision will be calculated from the two field duplicate samples using Relative Percent Difference (RPD) calculated as

$$\frac{(C1 - C2) \times 100}{(C1 + C2)/2} = \text{RPD}$$

where C1 = the larger of the two values and C2 = the smaller of the two values. The RPD for each analysis will be calculated for each duplicate pair.

Accuracy is a measure of bias that exists in a measurement system. Accuracy will be assessed through the analysis of matrix/matrix spike duplicate (MS/MSD) samples. The laboratory will determine method detection limits as per 40 CFR Part 136 for those parameters they are required to analyze MS/MSD. The analytical accuracy will be expressed as the percent recovery (%R) of an analyte which has been added to the environmental sample at a known concentration before analysis and is calculated according to the following

equation.

$$\%R = 100 \times \frac{S-U}{C_{S2}}$$

where: %R = percent recovery

S = measured concentration in spiked aliquot

U = measured concentration in unspiked aliquot

C<sub>S2</sub> = actual concentration of spike added

**Matrix/matrix spike duplicate analyses will be performed on 10% of the sites on each sampling occasion.** MS/MSDs will be analyzed for sulfate, chloride, (NO<sub>2</sub> + NO<sub>3</sub>)-N, total phosphorous, TOC, DOC, total metals and dissolved metals. MS/MSDs are also a measure of laboratory precision. The laboratory will develop acceptance /control criteria for precision (RPD) and MS/MSDs (%R and RPD). Any data with unacceptable QC checks should be flagged for having unacceptable QC.

**Field and equipment (filtration device) blanks will be collected once each day by each field crew.** The laboratory will also prepare and analyze a method blank for each set of samples prepared and analyzed. When analytical results for these blanks exceeds 1/10th of the values reported in the environmental samples, that data will be flagged as an estimate value due to blank contamination.

Comparability in the methods will be handled by using consistent field and lab methods. The inspectors who will be collecting the samples will be instructed in the standard protocol for collecting samples by George Kincaid of the Corps of Engineers. The same inspectors will be instructed in standard methods for measuring stream flow by representatives from the U.S. Geological Survey.

Completeness is a quality assurance/quality control term and is defined as the measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. Completeness will be judged on whether all samples are collected and analyzed with valid results. The limiting factors will be gaining access ahead of time, the weather, and flow limitations. The WVDEP mining inspectors are critical to gaining access to many of the sites which are on coal company property. Samples will be collected at all sites unless the streams are dry or we can't gain access. Completeness is calculated according to the following equation.

$$\% C = 100 \times \frac{V}{N}$$

where %C = percent completeness

V = number of measurements judged valid

N = total number of measurements necessary to achieve a specified statistical level of confidence in decision making.

The goal for this project is 90% completeness, however due to natural variations in environmental



conditions (such as weather and flow limitations), it is not possible to assure this goal will be met.

## 11. References

### Sampling Procedures:

US Department of Interior, Bureau of Reclamation *Water Measurement Manual*, 1967.

Operation Manuals for field meters regarding calibration procedures.

*NPDES Compliance Inspection Manual*, September 1994, EPA Publication 300-B-94-014.

### Laboratory Procedures:

40 CFR Part 136, *Guidelines Establishing Test Procedures for the Analysis of Pollutants*, July 1999.

*METHODS FOR CHEMICAL ANALYSIS OF WATER AND WASTES*, EPA-600/4-79-020, March 1983.

American Public Health Association, *Standard Methods*, 18<sup>th</sup> edition 1992.

## 12. Sample Custody Procedures

Samples will be collected by inspectors and preserved and stored in ice chests until they are shipped. The ice chests will be maintained under chain-of-custody by the sampler until packing for shipping is completed. Shipping containers will be sealed for transportation by Federal Express to the laboratory. The sample custodian at the laboratory will open the shipping containers and log in the samples following the custody-of-custody procedures in the lab until the analyses are completed. Once the results have been reported to the client, the remaining samples will be discarded.

## 13. Calibration Procedures and Preventative Maintenance

All instruments requiring calibration will be **calibrated at the beginning of the day of use** as a minimum. Field measurements will be taken for temperature, dissolved oxygen, conductivity and pH using an electrometric field meter. The results will be recorded on the field sheet for the next sample (see Appendix A). Analytical instruments (field and laboratory) are to be calibrated at the frequency specified by the analytical methods listed in the parameter table (but at least once per day) and by the procedures detailed in the methods listed in Table 2.

All calibrations (field and laboratory) will be fully documented and the records retained.

**All analytical instruments (laboratory) will have the daily calibration verified after every set of**

**20 or less samples using a calibration check standard** (mid-level calibration standard). The result obtained is to be within **20%** of the true value or the instrument is to be re-calibrated.

The laboratory shall define its **Quantitative Limits (QLs)** as the concentration of the lowest calibration standard employed for (NO<sub>2</sub>+ NO<sub>3</sub>)-N ; TP; TOC; and DOC; Chloride; and Sulfate. The QL for total/dissolved metals should not be less than 3 times the laboratory's established MDL for that analyte. Values below the QL must be reported as estimated values (with less certainty than those within the calibration range of the instrument). Values below the laboratory's determined MDLs be reported as less than the MDL concentration.

#### **14. Documentation, Data Reduction and Reporting**

Field data sheets will be retained by the laboratory. The raw data will be entered into a spread sheet and reported to Hope Childers at the EPA Wheeling Office. She will compile an ACCESS database of the chemical information for use in data interpretation and presentation in the report. She will also communicate this information to others including the WVDEP GIS staff and the EIS report contractor. She will also manage the records so they are suitable for long term data management.

#### **15. Data Validation**

Prior to reporting analytical results the laboratory will have ten percent of all the analytical results verified by a second analyst/supervisor by recalculation from the raw data to the final results.

The data will be used to determine the concentration of analytes relative to WV stream criteria/limits, and to compare concentrations of basic water quality parameters between streams adjacent to Valley Fill areas and those not near such potential impacts. Based upon the intended data use, the necessary method detection limits in the parameter table were selected, which in turn helped focus the selection of the analytical methods to those listed in the same table (those having the necessary sensitivity).

All data from stations MT 03, 15, 24, and 32 for the following ten analytes: sulfate, (NO<sub>2</sub>+NO<sub>3</sub>)-N, TOC, DOC, total iron, total aluminum, total manganese, dissolved iron, dissolved aluminum, and dissolved manganese will be recalculated by staff from OASQA. The Project Officer, will work with OASQA staff and the supporting laboratory if changes are needed in the selected stations or the critical analytes as the study progresses, e.g., selected stream has too low of flow during a given dry period. OASQA staff will provide a summary narrative of this data verification (findings, impact, recommendations) to the Project Officer. In addition, as part of the validation, staff of OASQA will review the overall report/ report deliverables for consistency with this Work plan. OASQA staff will provide a summary narrative (findings, impact, recommendations) to the Project Officer. The Project Officer will monitor the validation reports and follow-up with the laboratory performing the analytical work to assure correction of any problems.

Data transference is routinely checked and validated by laboratory personnel. Any problems will be

documented, described, data flagged and presented in the laboratory reports. Many of the streams may be very difficult to sample due to dry weather. Samples collected from stream sites that are difficult to sample due to extreme high or low flows may not be typical or representative of the true condition of the stream. These samples will be collected, processed, and analyzed, but they will be flagged, qualifying the results due to the difficult sampling conditions. The Project Officer will determine whether the data appear to be atypical or not representative of stream conditions, based on data collected at the same site in other seasons.

## **16. Performance and System Audits**

At least one field audit will be scheduled and conducted by the Wheeling Field Office to assure the sampling and field measurements are consistent with this plan. The Project Officer will make sure that the required number of field duplicates, MS/MSDs and field blanks are being collected. Any problems will be addressed and corrected to be in accordance with this project plan.

The Project Officer is to obtain a copy of the last WV Department of Environmental Protection on-site laboratory inspection report and follow-up correction report/s for the laboratory that will be employed for this project. The Project Officer is to obtain a copy of the results from the last three proficiency testing studies associated with the WV DEP certifications for the laboratory that will be employed for this project.

## **17. Corrective Action**

Repair and/or replacement of equipment and supplies will take place as needed.

Any changes to the original sampling plan will be documented in the final report.

Field duplicate samples will be analyzed as soon as possible following sampling events to identify any problems with the field sampling protocols, laboratory protocols, or personnel. Problems will be resolved as necessary and documented for the final report.

## **18. Reports**

The data reports from the laboratory will be sent to the EPA Wheeling Office. The following additional items will be included in each laboratory report: Name and location of laboratory; signature of the Laboratory Director (approval signature); project name; report date; stations; date and time of sampling; laboratory sample ID; listing of all problematic quality control items (for that set of samples) and supporting documentation of the necessary corrective action/s; analytical methods used for each parameter; date of analysis for each analyte; units; analytical results; results for laboratory and field blanks (field blanks are identified by samplers to the lab); sequential page number with total number of pages indicated; fully defined header information with tables of QC results; QC acceptance limits for each QC result; results of

preservations checks; MDLs for each analyte and referenced procedure; the QC results summary in each data package is to be limited to that associated with the samples in a months data package; the date and time or position in the analysis sequence of the analysis of QC sample (included in each QC sample result summary for each month); quantitation limits and a reference to method for establishing the QL (e.g.  $\geq 3 \times \text{MDL}$ ); and all calibration, analysis run logs, and sample “raw data” (instrument readings) for the key sites and parameters listed in Section 15, to allow the reconstruction of the analytical results, as part of data validation for this project. Additional supporting analytical data may be requested if problems are encountered in performing the data validation.

The final report will include the results of the project, any QA/QC problems encountered during the project; changes in the QAPP; and data quality assessment in terms of precision, accuracy, representativeness, completeness, and comparability. The final QAPjP will not be revised; any deviations from the original QAPP will be reported in the final report.

The Project Officer will be responsible for the completion and delivery of the final reports.

#### **Deliverable Time Line:**

The final report/package for October, November and December sampling is due June 13, 2000 to Project Officer. The final report/package for January sampling is due June 20, 2000. Final report/package for February sampling is due June 27, 2000. The final report for March sampling is due July 4<sup>th</sup>. The time line for the remaining data reports will be revisited by the Project Officer during July 2000.

## APPENDIX A.

### FIELD SHEET - WATER SAMPLING

STATION NUMBER \_\_\_\_\_ LOCATION \_\_\_\_\_  
DATE mm/dd/yy \_\_\_\_/\_\_\_\_/\_\_\_\_ TIME (military) \_\_\_\_\_ hours  
INVESTIGATOR(S) \_\_\_\_\_ A  
AGENCY \_\_\_\_\_

#### FIELD READINGS: Meter Make & ID:

pH \_\_\_\_ Temperature \_\_\_\_\_ (C) Dissolved Oxygen (mg/L) \_\_\_\_.  
Conductivity (umhos/cm) \_\_\_\_\_  
Calibration Data: Time: \_\_\_\_ Initials: \_\_\_\_ [Note: Minimum of one calibration/day]  
pH Calibration (4.0) \_\_\_\_ (7.0) \_\_\_\_ (10.0) \_\_\_\_\_ (Enter pH readings)  
Conductivity Calibration (Conc. of Std. KCl \_\_\_\_\_), Reading: \_\_\_\_\_ umhos/cm  
D.O Calibration (Temp.) \_\_\_\_\_ (Air Calibration ), Reading: \_\_\_\_\_ [Meters are Auto Altitude]  
Thermometer: (Reference Temperature 0C, Ice Water), Reading: \_\_\_\_\_

**Note: A Reference Thermometer check to be conducted by WV DEP.**

#### FLOW RATE (Meter Make & ID):

\_\_\_ gauging sheet attached  
\_\_\_ measured with bucket & stopwatch @ \_\_\_\_\_ (volume) per \_\_\_\_\_ (seconds) = \_\_\_ liters/sec  
\_\_\_ other method - describe

#### SAMPLE CONTAINERS FILLED AT THIS SITE (“\*” Collect Field Duplicate, Mark spaces “x” as Collect)

\_\_\_ \_\_\_ \* 1L (plastic) no chemical preservation for TSS, TDS, Sulfate, Chloride, Acidity, Alkalinity.  
\_\_\_ \_\_\_ \* 250 mL (plastic) preserved with sulfuric acid to pH<2 for Total phosphorous, (NO<sub>2</sub>+NO<sub>3</sub>)  
\_\_\_ \_\_\_ \* 40 mL (glass) preserved with sulfuric acid to pH <2 for Total Organic Carbon.  
\_\_\_ \_\_\_ \* 40 mL (glass), filtered, preserved with sulfuric acid to pH <2 for Dissolved Organic Carbon.  
\_\_\_ \_\_\_ \* 500 mL (plastic) preserved with nitric acid to pH <2 for total metals and mercury.  
\_\_\_ \_\_\_ \* 250 mL (plastic), filtered preserved with nitric acid to pH <2 for dissolved metals.  
\_\_\_ No Dup. 250 mL (plastic) preserved with nitric acid to pH <2 for dissolved metals (**Filter Blank, 1/day per crew**).  
\_\_\_ No Dup. 40 mL (glass) preserved with sulfuric acid to pH <2 for Dissolved Organic Carbon (**Filter Blank, 1/day/crew**).

#### FIELD FILTRATION

The plastic syringe will be used to suck up a sample from the stream. A new disposable 0.45 micron filter will be screwed on to the syringe and the sample will be filtered into the sample container for shipment to the laboratory. A new syringe and filter will be used at each sample site. The field filtering will comply with the requirements of 40 CFR Part 136, Table IB, note 4. **Filter blanks** will be prepared with lab pure water poured into filtering syringes, dispensed through the filter into the container, and acidified (acid listed above).

#### Chain of Custody:

Sampler Signature \_\_\_\_\_ Date (dd/mm/yy) \_\_\_\_\_ Time (military ) \_\_\_\_\_ Hours  
Place the above listed samples in the shipping container and seal them for shipment to the lab.

Lab Representative Signature \_\_\_\_\_. Received the above listed samples into the laboratory

custody on Date (mm/dd/yy) \_\_\_\_\_ Time (military) \_\_\_\_\_ Hours.

***OBSERVATIONS:***

APPENDIX B

FIELD SHEET - FLOW MEASUREMENT

STATION NUMBER \_\_\_\_\_ LOCATION \_\_\_\_\_

DATE mm/dd/yy \_\_\_\_/\_\_\_\_/\_\_\_\_ TIME (military) \_\_\_\_\_ hours

INVESTIGATOR(S) \_\_\_\_\_ A

AGENCY \_\_\_\_\_

Distance From Bank	Depth of Water	Depth of Reading	Velocity


***OBSERVATIONS:***

